
Abstract

Conventional PU products usually prepared from petroleum derived polyols contain significant amount of organic solvents. Environmental concerns regarding volatile organic compounds (VOC) and hazardous air pollutants (HAPs), limited fossil resources and economic competitiveness have motivated academic and industrial researchers towards the enhanced use of renewable feedstock for the production of eco-friendly polyurethane materials. Thrust is more on vegetable oil based waterborne polyurethane dispersions (PUDs) due to their environmental friendly nature, low viscosity at high molecular weight, reduced material costs associated with organic solvent and good applicability in many fields especially as coatings and adhesives for automobiles, wood, leathers and textiles. However, all these PUDs contain dimethylol propionic acid (DMPA) as internal emulsifier, which leads to low phase compatibility between hard and soft segments and high film formation time. In addition, the resulting PUD coatings suffer from poor surface properties.

The aim of this thesis was to develop new DMPA free waterborne PU dispersions and its copolymer dispersions from cotton seed oil based ionizable polyols i.e. polyols which have both OH groups and ionizable groups for coating applications. The study includes synthesis of the ionizable polyols, their characterization and their utilization in developing waterborne anionic PUDs. The characterization of PUDs and their cured films using different techniques have also been carried out. In addition, the coating properties of the PUDs have also been investigated.

Maleated hydroxylated polyol, an ionizable polyol (MAHCSO) was synthesized by maleanization of hydroxylated cottonseed oil polyol (HCSO). This maleated polyol (MAHCSO) was employed to develop anionic waterborne PUDs through a prepolymer method. The prepolymer was synthesized from MAHCSO, IPDI and hexane diol and neutralized with different counter cations and dispersed in water, subsequently chain extended with different aliphatic dihydrazides. Three different series of PUDs have been developed by varying the (i) ionic content (ii) chain extender and (iii) counter cation. The significant effect of the ionic content of the polyol (MAHCSO), chain length of dihydrazides and hydroxy alkyl chains of counter cation on particle size distributions, zeta potential distributions and viscosities of final PUDs and physico-chemical, thermo-mechanical and coating properties of the cured PUD films were observed. It was observed that PUD-ADH with TEA counter cation and ionic content of 0.5

equiv. exhibited good storage stability, water contact angle, T_g and mechanical strength as well as coating properties.

As a next step, a series of novel, DMPA free, catalyst free, anionic waterborne polyurethane-imide (PUID) dispersions have been successfully synthesized by using above mentioned maleated cottonseed oil polyol (MAHCSO) as an ionic soft segment, TDI as isocyanate and dianhydride as chain extenders. Three different aromatic dianhydrides were employed as chain extenders to introduce the imide functionality in the polyurethane hard segment and their effect on thermo-mechanical properties and phase compatibility between hard and soft segments were investigated. The cured films were characterized by different techniques including FT-IR (ATR), TGA, DMTA, UTM, and contact angle measurements. It was found that the tensile properties, thermal stability, water contact angle, and T_g values of PUIDs were remarkably high compared to neat PUD.

In an attempt to introduce other ionic groups in the polyol, phosphorylated polyols (phospol-P5, P10 and P15) bearing both hydroxyl and ionizable phosphoryl groups were synthesized through the ring opening hydrolysis of epoxy cottonseed oil (ECSO) with different concentrations of *ortho* phosphoric acid. Three different phosphols were synthesized and used for the development of a novel class of DMPA free and catalyst free anionic waterborne PUDs through a sol-gel technique using IPDI and 3-aminopropyl triethoxysilane (APTES). The obtained phosphols were characterized by ^1H NMR, FTIR, hydroxyl value, acid value, gel permeation chromatography (GPC) and rheological studies. The synthesized PUDs and their cured films were characterized by different techniques including zeta sizer, FTIR (ATR), Solid state ^{29}Si NMR, TGA, DMTA, DSC, and UTM. The hydrophobic nature of the films was measured by contact angle technique and their anti corrosion performance was studied through polarization technique. The films of PUD-P5 exhibited the highest tensile strength, thermal stability, T_g , contact angle and good anticorrosive properties due to the high degree of siloxane crosslinking.

In the next approach, an ionizable polyol was synthesized by ring opening of epoxidized cottonseed oil (ECSO) with 4-aminobenzoic acid (PABA) and blended with hydroxylated cottonseed oil polyol (HCSO) in different weight ratios to give mixed polyols having different hydroxyl numbers viz., 131, 118 and 106 mg KOH/g. Three different PUDs were synthesized using the mixed polyols, IPDI and 3-aminopropyltriethoxysilane. The chemical structure,

thermo-mechanical properties and surface properties of cured PUD films were examined using FTIR, TGA, DMTA and contact angle measurements. The effect of Si—O—Si cross-linking density, which increases with increasing OH values of the mixed polyol, was also investigated. All the PUDs prepared in this study exhibited good storage stability (> 4 months), and the average particle sizes of PUDs ranged from 18 to 124 nm. The PUD film (PUD-35 film) prepared with mixed polyol having the highest hydroxyl value exhibited high thermal stability, mechanical strength; T_g , water contact angle value, chemical, abrasion and scratch resistance due to the extensive siloxane cross-links.

List of Schemes

- Scheme 1.1a** General reaction mechanism of urethane formation
- Scheme 1.1b** General reaction mechanism of polyurethane formation
- Scheme 1.2** General schematic representation of anionic waterborne PUDs
- Scheme 1.3** General schematic representation of cationic waterborne PUDs
- Scheme 1.4** Chain extension of NCO terminated PU prepolymer with water
- Scheme 1.5** Chain extension of NCO terminated PU prepolymer with amine chain extender
- Scheme 1.6** Synthesis of PUDs using acetone process
- Scheme 1.7** Synthesis of waterborne PUDs *via* prepolymer mixing process
- Scheme 1.8** Synthesis of waterborne PUDs *via* hot-melt process
- Scheme 1.9** General representation of ketimine-ketazine process
- Scheme 2.1** Synthesis of HCSO through *in situ* epoxy ring opening of ECSO
- Scheme 2.2** Synthesis of MAHCSO through Maleanization of HCSO
- Scheme 2.3** Preparation of PUDs with different chain extenders
- Scheme 2.4** Preparation of PUDs with different neutralizing agents
- Scheme 3.1** Synthesis of waterborne PU-imide dispersions
- Scheme 3.2** Types of hydrogen bonding (**a**) between hard segment (HS) and hard segment (HS), and (**b**) between hard segment (HS) and soft segment (SS) in PU-imides.
- Scheme 4.1** Synthesis of phospols from ECSO
- Scheme 4.2** Schematic route for the preparation of PUDs
- Scheme 5.1** Synthesis of ionizable polyol from ECSO
- Scheme 5.2** Synthesis of anionic waterborne PUDs

List of Figures

Figure: 1.1 Global PUD market, 2014-2020.

Figure 1.2 Schematic representation of polyurethane-urea anionomer exhibiting phase separation involving hard and soft segments and interactions between different moieties

Figure 1.3 Electrostatic stabilization mechanisms of PUD particles

Figure 1.4 Film formation process of a PUD

Figure 1.5 General internal emulsifiers utilized in PUD preparation

Figure 1.6 Different di & polyamine chain extenders used in the synthesis of PUDs

Figure 1.7 Global PUD market share by applications-2012

Figure 1.8 CSO production in India by year

Figure 1.9 Structures of some vegetable oil based ionic soft segments

Figure 2.1 FTIR spectra of ECSO, HCSO and MAHCSO

Figure 2.2 ^1H NMR spectra of HCSO and MAHCSO

Figure 2.3 Appearance of dispersions with different chain extenders (a) PUD-ODH (b) PUD-SDH (c) PUD-ADH (d) PUD-SBDH and their cured films

Figure 2.4 Appearance of dispersions with different counteractions (a) PUD-TEA (b) PUD-DMEA (c) PUD-NMDA (d) PUD-TEOA and their cured films

Figure 2.5 Particle size distributions of PUDs (a) with different chain extenders, (b) with different ionic contents

Figure 2.6 Viscosity of PUDs (a) with different chain extenders, (b) with different ionic contents

Figure 2.7 (a) Particle size distributions, (b) Zeta potential distribution of PUDs with different counteractions

Figure 2.8 Electrolytic stability of PUDs with (a) different chain extenders (b) different counteractions

Figure 2.9 FTIR spectra of PUD films with different chain extenders

Figure 2.10 FT-IR spectra of (a) PUD films (b) PU prepolymer.

Figure 2.11 Temperature dependence of (a) storage modulus and (b) $\tan \delta$ of PU dispersions

Figure 2.12 Temperature dependence of (a) storage modulus and (b) $\tan \delta$ of PU dispersions

Figure 2.13 Water contact angle values of PUD films with different chain extenders

Figure 2.14 Water contact angle values of PUD films with different counteractions

Figure 2.15 Specimens of PUD-ADH coating on mild steel panel before and after abrasion resistance test

Figure 2.16 Specimens of PUD-ADH coating on galvanized steel panel before and after flexural testing

Figure 3.1 Visual appearances of dispersions (a) PUD, (b) PUID-PMDA, (c) PUID-BPOTCDA, (d) PUID-HFIDA and their cured films

Figure 3.2 Particle size distributions of PU and PU-imide dispersions

Figure 3.3 FTIR spectra of films (a) PUD, (b) PUID-PMDA, (c) PUID-BPOTCDA, (d) PUID-HFIDA.

Figure 3.4 Temperature dependence of (a) E' and (b) $\tan \delta$ of PUD and PU-imide films

Figure 3.5 TGA curves of PUD and PUID films

Figure 3.6 Stress-strain curves for PUD and PU-imide films

Figure 3.7 Water contact angle values of PUD and PUID films.

Figure 3.8 Specimens of PUID-HFIPDA coating on mild steel panel before and after abrasion resistance test

Figure 3.9 Specimens of PUD coating on mild steel panel before and after abrasion resistance test

Figure 3.10 Specimens of PUID-HFIDA coating on galvanized steel panel before and after flexural testing

Figure 3.11 Specimens of PUD coating on galvanized steel panel before and after flexural testing

Figure 4.1 Appearance of phospols

Figure 4.2 Viscosity-temperature relationship for CSO-phospols

Figure 4.3 FT-IR spectra of (a) ECSO and phospol (b) phospol-P5, P10, and P15

Figure 4.4 ^{31}P NMR spectra of phospols

Figure 4.5 ^1H NMR spectra of ECSO and phospol

Figure 4.6 Appearance of dispersions (a) PUD-P5 (b) PUD-P10 (c) PUD-P15 and their cured films

Figure 4.7 Particle size distributions of PUDs

Figure 4.8 Probable mechanism of Phospol-PUD film curing process through the formation of siloxane cross-links

Figure 4.9 FT-IR spectra of cured films of PUD-P5, P10, and P15

-
- Figure 4.10** Solid state ^{29}Si NMR of PUD-P5 film
- Figure 4.11** Temperature dependence of E' and $\tan \delta$ of PUD films
- Figure 4.12** DSC scans of PUD films
- Figure 4.13 (a)** TGA **(b)** derivative TGA curves of PUD films
- Figure 4.14** Water contact angle values of PUD films
- Figure 4.15** Tafel polarization of (a) MS bare, (b) PUD-P15, (c) PUD-P10, and (d) PUD-P5 in 3.5 wt% NaCl
- Figure 4.16** Schematic representation of corrosion protection in phospor PUDs
- Figure 4.17** Specimens of PUD-P5 coating on mild steel panel before and after abrasion resistance test
- Figure 4.18** Specimens of PUD-P5 coating on galvanized steel panel before and after flexural testing
- Figure 5.1** FTIR spectra of ECSO and ionizable polyol
- Figure 5.2** ^1H NMR spectra of ECSO and ionizable polyol
- Figure 5.3** Appearance of dispersions (a) PUD-35 (b) PUD-50 (c) PUD-65 and their cured films
- Figure 5.4** Particle size distribution of PUDs
- Figure 5.5** ATR-FTIR spectra of cured PUD films
- Figure 5.6** Temperature dependence of **(a)** E' and **(b)** $\tan \delta$ of PUD films
- Figure 5.7 (a)** TGA and **(b)** derivative TGA curves of PUD films
- Figure 5.8** Stress-strain curves of PUD films
- Figure 5.9** Water contact angles of PUD films
- Figure 5.10** Specimens of PUD-35 coating on mild steel panel before and after abrasion resistance test.
- Figure 5.11** Specimens of PUD-35 coating on galvanized steel panel before and after flexural testing

List of Tables

- Table 2.1** Properties of HCSO and MAHCSO
- Table 2.2** Chemical composition of PUDs with different chain extenders
- Table 2.3** Chemical composition of PUDs with different counteractions
- Table 2.4** Characteristic properties of PUDs with different chain extenders
- Table 2.5** Characteristic properties of PUDs with different counteractions
- Table 2.6** Intensity of —NH stretching & —CH_2 stretching in PUD films
- Table 2.7** Visco-elastic properties of PUD films with different chain extenders
- Table 2.8** Visco-elastic properties of PUD films with different counteractions
- Table 2.9** Tensile properties of PUD films with different chain extenders
- Table 2.10** Tensile properties of PUD films with different counteractions
- Table 2.11** Chemical and solvent resistance of PUD films with different chain extenders
- Table 2.12** Chemical and solvent resistance of PUD films with different counteractions
- Table 3.1** Chemical composition of PUD and PUIDs
- Table 3.2** Characteristic properties of PUD and PUIDs
- Table 3.3** Visco-elastic properties of PUD and PUID films
- Table 3.4** TGA data of PUD and PUID films
- Table 3.5** Tensile properties of PUD and PUID films
- Table 3.6** Chemical and solvent resistance of PUD and PUID films
- Table 4.1** Characteristic properties of Phospols
- Table 4.2** Chemical composition of PUDs
- Table 4.3** Characteristic properties of PUDs
- Table 4.4** Thermal (DMTA, DSC & TGA) properties of PUD films
- Table 4.5** Tensile properties of PUD films
- Table 4.6** Tafel polarization data of coated and uncoated MS in 3.5% NaCl
- Table 4.7** Chemical and solvent resistance of PUD films
- Table 5.1** Characteristic properties of ionizable polyol
- Table 5.2** Chemical composition of PUDs
- Table 5.3** Characteristic properties of PUDs
- Table 5.4** Thermal (DMTA & TGA) properties of PUD films
- Table 5.5** Tensile properties of PUD films
- Table 5.6** Chemical and solvent resistance of PUD films

List of Abbreviations

ADH	Adipic dihydrazide
APTES	Aminopropyl triethoxysilane
AV	Acid value
E_{ac}	Activation energy
BPOTCDA	Benzophenone-tetracarboxylic dianhydride
CHDM	Cyclohexane-1,6-dimethylol
E_{corr}	Corrosion potential
I_{corr}	Corrosion current
DMEA	Dimethylethanolane
DHZ	Dihydrazide
DMPA	Dimethylol propanoic acid
DMF	Dimethylformamide
DMTA	Dynamic mechanical and thermal analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogram
ECISO	Epoxidized cottonseed oil
EA	Ethyl acetate
ε	Elongation at break
FA	Formic acid
FT-IR	Fourier transform infrared
g	Grams
GPC	Gel permeation chromatography
T_g	Glass transition temperature
HCSO	Hydroxylated cottonseed oil
HDO	Hexane 1,6-diol
HFIPDA	Hexafluoroisopropylidene-diphthalic anhydride
HV	Hydroxyl value
HSC	Hard segment content
IPDI	Isophorone diisocyanate
MAHCSO	Maleated hydroxylated Cottonseed oil

MA	Maleic anhydride
MEK	Methyl ethyl ketone
mg	Milligram
MS	Mild steel
MHz	Megahertz
mL	Millilitre
MPa	Megapascal
NMDA	<i>N</i> -Methyl diethanolamine
NMR	Nuclear magnetic resonance
N	Normality
nm	Nano meter
M_n	Number average molecular weight
ODH	Oxalic dihydrazide
OOC	Oxirane oxygen content
Phospol	Phosphorylated polyol
PABA	Para-aminobenzoic acid
PMDA	Pyromellitic dianhydride
PU	Polyurethane
PUD	Polyurethane dispersion
PUID	Polyurethane-imide dispersion
PDI	Polydispersity index
SDH	Succinic dihydrazide
SBDH	Sebacic dihydrazide
E'	Storage modulus
TEA	Tri ethyl amine
TEOA	Triethanolamine
TDI	Toluene diisocyanate
TGA	Thermo gravimetric analysis
σ	Tensile strength
UTM	Universal testing machine
M_w	Weight average molecular weight
E	Young's modulus

